Claims

1. An aqueous composition useful for an anodizing of a surface of magnesium or of a magnesium alloy comprising:
   i. phosphorus and oxygen containing anions;
   ii. at least one water-soluble inorganic hydroxide;
   iii. at least one surfactant; and
   iv. at least one alcohol having at least one alkaline radical group, at least one hydrolyzed alkaline silane or a mixture of them,
   v. wherein the pH of the composition is greater than 7.

2. The composition of claim 1 wherein the phosphorus and oxygen containing anions are selected from the group consisting of mono-, di-, tri-P containing groups like in an orthophosphate, hydrophosphate or pyrophosphate and of a six P atoms containing group like in a hexametaphosphate.

3. The composition of claim 1 wherein the concentration of phosphorus and oxygen containing anions in the anodizing solution is in the range from 0.001 to 6.0 M, calculated as PO_4.

4. The composition of claim 1 wherein the concentration of phosphorus and oxygen containing anions in the anodizing solution is in the range from 0.01 to 100 g/L, calculated as PO_4.

5. The composition of claim 1 wherein the at least one water-soluble inorganic hydroxide comprises a content of NH_4OH, LiOH, NaOH, KOH or any mixture of them.

6. The composition of claim 1 wherein the at least one water-soluble inorganic hydroxide is selected from the group consisting of NH_4OH, LiOH, NaOH, KOH and any mixture of them.

7. The composition of claim 1 wherein the concentration of the water-soluble inorganic hydroxides in the anodizing solution is in the range from 0.2 M to 4 M.

8. The composition of claim 1 wherein the concentration of the water-soluble inorganic hydroxides in the anodizing solution is in the range from 0.01 to 100 g/L.

9. The composition of claim 1 wherein the at least one surfactant is selected from the group consisting of amphoteric surfactants, anionic surfactants and non-ionic surfactants.

10. The composition of claim 1 wherein the non-ionic surfactant is selected from ethoxylated alkylalcohols, ethoxylated-propoxylated alkylalcohols, ethoxylated alkylalcohols with end group locking and ethoxylated-propoxylated alkylalcohols with end group locking, ethoxylated alkylphenols, ethoxylated-propoxylated alkylphenols, ethoxylated alkylphenols with end group locking and ethoxylated-propoxylated alkylphenols with end group locking, ethoxylated alkylamines, ethoxylated alkanic acids and ethoxylated-propoxylated alkanic acids and blockcopolymers comprising at least one polyethylene oxide block and at least one polypropylene oxide block.

11. The composition of claim 1 wherein the surfactant is a non-ionic surfactant having 3 to 100 monomeric groups selected from ethylene oxide and propylene oxide monomeric groups with up to 15.000 carbon atoms, whereby the long chain may be one chain, a double chain, a multiple of chains, a regular or irregular arrangement of ethylene oxide monomeric groups, propylene oxide monomeric groups, a block copolymer or their combinations, whereby the chains may be straight chains without or with bigger side groups, whereby the surfactant may optionally have an alkyl group with 6 to 24 carbon atoms.

12. The composition of claim 1 wherein the surfactant is a non-ionic surfactant which is selected from alkylpolyglucosides having an alkyl group – saturated or unsaturated – with an average number of carbon atoms in the range from 4 to 18 in each chain and having at least one chain which may be independent one from the other a linear or a branched chain and having an average number of 1 to 5 units of at least one glucoside, whereby the units of the at least one glucoside may be bound glucosidically to the alkyl group.

13. The composition of claim 1 wherein said surfactant is a polyoxyalkylene ether.

14. The composition of claim 1 wherein said surfactant is selected from the group consisting of polyoxyethylene oleyl ethers, polyoxyethylene cetyl ethers, polyoxyethylene stearyl ethers and polyoxyethylene dodecyl ethers.

15. The composition of claim 1 wherein said surfactant is polyoxyethylene(10)oleyl ether.

16. The composition of claim 1 wherein the surfactant is an anionic surfactant having an alkyl group – saturated or unsaturated – with an average number of carbon atoms in the range from 6 to 24 in each chain and having at least one chain which may be independent one from the other a linear or a branched chain and having optionally an alkyl part of the molecule with one or more aromatic groups and having at least one sulfate group per molecule, at least one sulfonate group per molecule or at least one sulfate group and at least one sulfonate group per molecule.

17. The composition of claim 1 wherein the surfactant is an anionic surfactant (ether sulfate) selected from the group consisting of ethoxylated alkylalcohols, ethoxylated-propoxylated alkylalcohols and their mixtures having a sulfate group whereby the alkyl group of the

alkylalcohols – saturated or unsaturated – has an average number of carbon atoms in the range from 6 to 24 in each chain and having at least one chain which may be independent one from the other a linear or a branched chain, whereby each ethylene oxide chain may have an average number of 2 to 30 ethylene oxide units, whereby there may be at least one propylene oxide chain having an average number of 1 to 25 propylene oxide units, whereby the alkyl part of the molecule may optionally show one or more aromatic groups, one or more phenolic groups or a mixture of at least one aromatic group and at least one phenolic group.

18. The composition of claim 1 wherein the surfactant is an anionic surfactant (ether phosphate) selected from the group consisting of ethoxylated alkylalcohols, ethoxylated-propoxylated alkylalcohols and their mixtures having a phosphate group, whereby the alkyl group of the alkylalcohols – saturated or unsaturated – has an average number of carbon atoms in the range from 6 to 24 in each chain and having at least one chain which may be independent one from the other a linear or a branched chain, whereby each ethylene oxide chain may have an average number of 2 to 30 ethylene oxide units, whereby there may be at least one propylene oxide chain having an average number of 1 to 25 propylene oxide units, whereby the alkyl part of the molecule may optionally show one or more aromatic groups, one or more phenolic groups or a mixture of at least one aromatic group and at least one phenolic group.

19. The composition of claim 1 wherein the surfactant is an anionic surfactant selected from the group consisting of phosphate esters having one or two alkyl groups each independent one from the other – saturated or unsaturated – which have an average number of carbon atoms in the range from 4 to 18 in each chain and having at least one chain which may be independent one from the other a linear or a branched chain, whereby the alkyl part of the molecule may optionally show one or more

aromatic groups, one or more phenolic groups or a mixture of at least one aromatic group and at least one phenolic group, whereby there is one phosphate group in each molecule.

20. The composition of claim 1 wherein the surfactant is an amphoteric surfactant which may be selected from the group consisting of amine oxides, betaines and protein hydrolyzates.

21. The composition of claim 1 wherein the concentration of the surfactants in the anodizing solution is in the range from 0.005 to 3 g/L.

22. The composition of claim 1 wherein the at least one alcohol showing at least one alkaline radical group is selected from alcohols showing in an aqueous solution a pH of at least 9.

23. The composition of claim 1 wherein the at least one alcohol showing at least one alkaline radical group is selected from the group consisting of alkaline compounds showing at least one amido group, at least one amino group, at least one imino group, at least one imido group, at least one ureido group or any mixture of them.

24. The composition of claim 1 wherein at least one alcohol showing at least one alkaline radical group is at least one compound selected from the group consisting of mono-, di-, tri-alkanolamines and of amino-methyl propanol, amino-ethyl propanol, 2-amino-2-methyl-1-propanol and amino-propyl propanol.

25. The composition of claim 1 wherein the concentration of the alcohols showing at least one alkaline radical group in the anodizing solution is in the range from 1 ml/l to 100 ml/l.

26. The composition of claim 1 wherein the concentration of the alcohols showing at least one alkaline radical group in the anodizing solution is in the range from 1 g/L to 100 g/L.

27. The composition of claim 1 wherein the alkaline hydrolyzed silane is selected from silanes having at least one amino group, having at least one ureido group, having at least one imino group and of mixtures of these silanes.

28. The composition of claim 1 wherein the alkaline hydrolyzed silane is selected from the group consisting of:

aminoalkyltrialkoxysilanes,
aminoalkylaminoalkyltrialkoxysilanes,
triaminofunctional silanes,
bis-trialkoxysilylalkylamines,
(gamma-trialkoxysilylalkyl)dialkylentriamin,
N-(aminoalkyl)-aminoalkylalkyldialkoxysilanes,
N-phenyl-aminoalkyltrialkoxysilanes,
N-alkyl-aminoisoalkyltrialkoxysilanes,
4-amino-dialkylalkyltrialkoxysilanes,
4-amino-dialkylalkylalkyldialkoxysilanes,
polyaminoalkylalkyldialkoxysilan
ureidoalkyltrialkoxysilanes and
their corresponding silanols and siloxanes.

29. The composition of claim 1 wherein the at least one hydrolyzed alkaline silane is selected from the group consisting of silanes, silanols and siloxanes corresponding to silanes having at least one amino group, at least one imino group, at least one ureido group and of mixtures of these silanes, silanols and siloxanes.

30. The composition of claim 1 wherein the concentration of the hydrolyzed alkaline silanes in the anodizing solution is in the range from 0.1 ml/l to 50 ml/l.

31. The of claim 1 wherein the concentration of the hydrolyzed alkaline silanes in the anodizing solution is in the range from 0.1 g/L to 50 g/L.

32. A method of treating the surface of a metallic workpiece comprising the steps of:
    a) providing a surface of at least one metal, of at least one alloy or of a mixture of them, whereby at least one of the metals and alloys is anodizable that is used as an electrode;
    b) contacting said metallic surface with an anodizing solution;
    c) providing at least one other electrode in contact with said anodizing solution; and
    d) passing an electric current between said metallic surface and said other electrode through said anodizing solution,
    e) wherein said anodizing solution is an aqueous solution having a pH greater than 7 and comprising:
        i. phosphorus and oxygen containing anions;
        ii. at least one water-soluble inorganic hydroxide;
        iii. at least one surfactant; and
        iv. at least one alcohol showing at least one alkaline radical group or at least one alkaline hydrolyzed silane or a mixture of them.

33. The method of claim 32 comprising the steps of:
    a) providing a surface of at least one metal, of at least one alloy or of a mixture of them, of which at least a part of the metals, alloys or their combinations is selected from the group consisting of magnesium, magnesium alloy, aluminum, aluminum alloy, titanium, titanium alloy, beryllium and beryllium alloy that is used as an electrode;

b) contacting said surface with an anodizing solution;
c) providing at least one other electrode in contact with said anodizing solution; and
d) passing an electric current between said metallic surface and said other electrode through said anodizing solution,
e) wherein said anodizing solution is an aqueous solution having a pH greater than 7 and comprising:
    i. phosphorus and oxygen containing anions;
    ii. at least one water-soluble inorganic hydroxide;
    iii. at least one surfactant; and
    iv. at least one alcohol showing at least one alkaline radical group or at least one alkaline hydrolyzed silane or a mixture of them.

34. The method of claim 32 comprising the steps of:
a) providing a surface of at least one metal, of at least one alloy or of a mixture of them, whereby at least one of the metals and alloys is anodizable that is used as an electrode;
b) immersing said surface with an anodizing solution;
c) providing at least one other electrode in contact with said anodizing solution; and
d) passing an electric current between said metallic surface and said other electrode through said anodizing solution,
e) wherein said anodizing solution is an aqueous solution having a pH greater than 7 and comprising:
    i. phosphate anions;
    ii. at least one water-soluble inorganic hydroxide;
    iii. at least one surfactant; and
    iv. at least one alcohol showing at least one alkaline radical group or at least one alkaline hydrolyzed silane or a mixture of them.

35. The method of claim 32 comprising the steps of:

a) providing a surface of at least one metal, of at least one alloy or of a mixture of them, of which at least a part of the metals, alloys or their combinations is selected from the group consisting of magnesium, magnesium alloy, aluminum, aluminum alloy, titanium, titanium alloy, beryllium and beryllium alloy that is used as an electrode;
b) immersing said surface in an anodizing solution;
c) providing at least one other electrode in contact with said anodizing solution; and
d) passing an electric current between said metallic surface and said other electrode through said anodizing solution,
e) wherein said anodizing solution is an aqueous solution with a pH greater than 7 and comprises:
    i. phosphate anions;
    ii. at least one water-soluble inorganic hydroxide;
    iii. at least one surfactant; and
    iv. at least one alcohol having at least one amino group or at least one alkaline hydrolyzed silane or a mixture of them.

36. The method of claim 32 wherein said workpiece is used as an anode for direct current or as an electrode for alternative current.

37. The method of claim 32 wherein there is a treatment of the surface of the workpiece with at least one cleaning solution, with at least one deoxidizer solution or with at least one cleaning solution and with at least one deoxidizer solution prior to contacting the surface with the anodizing solution.

38. The method of claim 32 whereby there may be applied at least one rinsing solution prior to or after the application of the anodizing solution.

39. The method of claim 32 wherein said current has a density of less than 4 A/dm^2 of said metallic surface.

40. The method of claim 32 further comprising the step: e. during said passing an electric current, maintaining said anodizing solution at a temperature of between 0 °C and 60 °C.

41. The method of claim 32 wherein a coating is prepared having an average coating thickness in the range from 2 to 50 µm.

42. The method of claim 32 wherein there is further applied at least one coating selected from the group consisting of coatings prepared from a solution containing at least one acid or from an alkaline solution containing e.g. at least one silane, prepared from a paint, prepared from a dispersion or solution containing at least one resin, prepared from a powder paint and prepared from electroless deposited metal like nickel rich coatings.

43. A method of treating the surface of a metallic workpiece having at least on a portion of the metallic surface an anodizable material whereby the method comprises the steps of:
    a) providing a surface of at least one metal, of at least one alloy or any combination of them, whereby at least one of the metals and alloys is anodizable that is used as an anode;
    b) contacting said metallic surface with an anodizing solution;
    c) providing at least one other electrode in contact with said anodizing solution; and
    d) passing an electric current between said metallic surface and said other electrode through said anodizing solution as an alternative current, a direct current or a current pulsed in any way,
    e) wherein a layer containing at least one non-conductive polymer is generated on the metallic surface in the earliest stage of the anodizing,

f) wherein the non-conductive polymer containing layer on the metallic surface provides an essential contribution in the initiation of the formation of micro-plasma arcs,
g) wherein the non-conductive polymer containing layer is transformed to a gel layer in which gel micelles are oriented according to the electromagnetic field,
h) wherein micro-plasma arcs are generated during anodizing,
i) whereby the micro-plasma arcs are provided as controlled micro-sparking regime,
j) wherein there is essentially no break-down of the coating or wherein there is essentially no formation of big pores - except in cases where impurities or inhomogeneities in the metallic surface cause a break-down or the formation of a big pore or both,
k) wherein the gel micelles are – at least partially – kept on distance one to the other,
l) wherein there are channels or gaps more or less directed rectangular to the metallic surface between at least some of the micelles,
m) wherein these channels or gaps are at least partially prevented to close during the anodizing and
n) wherein the anodizing layer is built up during the anodizing by decomposition of the gel layer and by oxidation of parts of the metallic surface.

44. An anodizing coating produced by a method as claimed in claim 32.

45. The coating as claimed in claim 44 having a composition comprising at least one metal phosphate, metal oxide and metal hydroxide whereby the at least one metal is selected from the metals contained in the metallic surface and comprising further at least one polymer.

46. The coating as claimed in claim 44 having a composition comprising at least one magnesium compound selected from magnesium phosphate,

magnesium oxide and magnesium hydroxide and comprising further at least one polymer.

47. The coating as claimed in claim 44 having a composition comprising magnesium phosphate, magnesium oxide, magnesium hydroxide, at least one polymer.

48. The coating as claimed in claim 44 having a composition comprising magnesium phosphate, magnesium oxide, magnesium hydroxide, at least one polymer and at least one compound reacted from at least one silane, at least one silanol or at least one siloxane.

49. The coating as claimed in claim 44 having a composition comprising at least 50 % by weight of at least one magnesium compound.

50. An anodizing coating produced by a method as claimed in claim 43.

51. The coating as claimed in claim 50 having a composition comprising at least one metal phosphate, metal oxide and metal hydroxide whereby the at least one metal is selected from the metals contained in the metallic surface and comprising further at least one polymer.

52. The coating as claimed in claim 50 having a composition comprising at least one magnesium compound selected from magnesium phosphate, magnesium oxide and magnesium hydroxide and comprising further at least one polymer.

53. The coating as claimed in claim 50 having a composition comprising magnesium phosphate, magnesium oxide, magnesium hydroxide, at least one polymer.

54. The coating as claimed in claim 50 having a composition comprising magnesium phosphate, magnesium oxide, magnesium hydroxide, at

least one polymer and at least one compound reacted from at least one silane, at least one silanol or at least one siloxane.

55. The coating as claimed in claim 50 having a composition comprising at least 50 % by weight of at least one magnesium compound.

56. An anodizing coating produced with the anodizing solution as claimed in claim 1.

57. The coating as claimed in claim 56 having a composition comprising at least one metal phosphate, metal oxide and metal hydroxide whereby the at least one metal is selected from the metals contained in the metallic surface and comprising further at least one polymer.

58. The coating as claimed in claim 56 having a composition comprising at least one magnesium compound selected from magnesium phosphate, magnesium oxide and magnesium hydroxide and comprising further at least one polymer.

59. The coating as claimed in claim 56 having a composition comprising magnesium phosphate, magnesium oxide, magnesium hydroxide, at least one polymer.

60. The coating as claimed in claim 56 having a composition comprising magnesium phosphate, magnesium oxide, magnesium hydroxide, at least one polymer and at least one compound reacted from at least one silane, at least one silanol or at least one siloxane.

61. The coating as claimed in claim 56 having a composition comprising at least 50 % by weight of at least one magnesium compound.

62. An anodizing coating having a thickness in the range from 8 to 30 µm generated in an anodic anodizing process formed on a surface of

magnesium or of a magnesium alloy that is not sealed with another coating (bare corrosion) having a corrosion resistance of less than 1 % area of corrosion on the flat surface after at least 300 h or after at least 336 h of exposition in 5 % NaCl salt spray test according to ASTM B 117.

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